

MENU

SEARCH

INDEX

DETAIL

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1 / 1

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(54) METHOD FOR SYNTHESIZING ACETOXYACETIC ACID

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a method for synthesizing acetoxyacetic acid economically, easier and under by using metal oxide catalyst carried with sulfuric acid derivatives moderate conditions.

SOLUTION: This method for synthesizing acetoacetic acid is characterized by reacting carbon monoxide, acetic acid and/or acetic anhydride with formaldehyde and/or a compound generating formaldehyde under a reaction condition in the presence of a metal oxide loaded with sulfuric acid group as a catalyst in a reaction medium.

JAPANESE

[JP,2001-335538,A]

CLAIMS DETAILED DESCRIPTION TECHNICAL
FIELD PRIOR ART EFFECT OF THE INVENTION
TECHNICAL PROBLEM MEANS EXAMPLE

[Translation done.]

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CLAIMS

[Claim(s)]

[Claim 1]In a synthetic method of acetoxyacetic acid, under existence of a sulfuric acid root support metallic oxide, A synthetic method of acetoxyacetic acid making carbon monoxide, acetic acid, and/or an acetic anhydride react to a compound which generates formaldehyde under formaldehyde and/or a reaction condition into a reaction medium.

[Claim 2]A synthetic method of the acetoxyacetic acid according to claim 1 which is at least one sort chosen from a group which a sulfuric acid root support metallic oxide becomes from sulfuric acid root support zirconia, a sulfuric acid root support titania, and sulfuric acid root support tin oxide.

[Claim 3]A synthetic method of the acetoxyacetic acid

according to claim 1 or 2 which is at least one sort chosen from a group which a reaction medium becomes from halogenated aliphatic hydrocarbon, halogenated aromatic hydrocarbon, aliphatic hydrocarbon, and aromatic hydrocarbon.

[Claim 4] A catalyst for composition of acetoxyacetic acid which consists of at least one sort chosen from a group which consists of sulfuric acid root support zirconia, a sulfuric acid root support titania, and sulfuric acid root support tin oxide.

[Translation done.]

JAPANESE

[JP,2001-335538,A]

CLAIMS DETAILED DESCRIPTION TECHNICAL FIELD PRIOR ART EFFECT OF THE INVENTION TECHNICAL PROBLEM
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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention relates to the synthetic method of acetoxyacetic acid (acetyl glycolic acid).

[0002]

[Description of the Prior Art]Acetoxyacetic acid is used as synthetic powder, when manufacturing various chemicals, such as agricultural chemicals and a finishing agent.

In the chemical industry, it is an important compound.

[0003]As a method of compounding acetoxyacetic acid, glycolic acid ethyl and acetic acid are heated with a small amount of sulfuric acid in benzene, There are a method (JP,56-63941,A) of making oxygen gas react to acetic acid under high temperature high pressure, etc. under three-ingredient coexistence of the method (Beilstein, 3, 233) of removing and compounding the water and the ethyl acetate which were produced, an alkali metal iodide, a metallic oxide or metal acetate, and iodine.

[0004]Since glycolic acid ethyl of a raw material is a substance which has inflammability by stimulateness, the former method is not easy handling and it is expensive. The separating operation of a catalyst and output becomes the number of reagents used since catalyst ability is not

demonstrated in the latter method unless it makes three ingredients live together increases, and complicated, There are problems, like also becoming a high cost and the yield of acetoxyacetic acid which is output is low (yield of acetoxyacetic acid in an example: 1%). Therefore, these methods cannot be said to be the method excellent in the industrial target.

[0005]JP,11-147042,A SiO₂ / aluminum₂O₃ mole ratio uses at least 100 or more mordenites by making aliphatic aldehyde and carbon monoxide into a catalyst, The manufacturing method of the hydroxycarboxylic acid derivative making it react in a reaction medium and obtaining a hydroxycarboxylic acid derivative" is indicated. It is indicated by the above-mentioned gazette that acetoxyacetic acid is compoundable as hydroxycarboxylic acid.

[0006]However, in this method, a temperature as high as 170-200 ** is required for reaction temperature especially to obtain 100-300 ** and high yield. When using a toxic high gas like carbon monoxide, the mild thing of a reaction condition is preferred. The mordenite of the mole ratio of SiO₂/aluminum₂O₃ high high silica type is dramatically

expensive compared with the usual mordenite.

[0007]As mentioned above, the method indicated in the above-mentioned gazette had a problem in respect of safety, economical efficiency, etc.

[0008]Thus, the conventional acetoxyacetic acid synthetic method had problems, like separation of the catalyst from reaction mixture or an objective product is difficult, or a severe reaction condition is required, or a raw material and a catalyst are expensive and there are.

[0009]

[Problem(s) to be Solved by the Invention]This invention solves the problem of the above conventional methods, and primarily aims to provide the method of compounding acetoxyacetic acid economically under a simpler more mild condition.

[0010]

[Means for Solving the Problem]By using a specific catalyst in which it is comparatively cheap and composition is easy as a result of repeating research wholeheartedly etc., this invention person finds out a method of compounding acetoxyacetic acid with good yield under a mild reaction condition, and came to complete this invention.

[0011]That is, this invention relates to a catalyst for composition of a synthetic method of the following acetoxyacetic acid, and acetoxyacetic acid.

In a synthetic method of acetoxyacetic acid, 1. Under existence of sulfuric acid root support metallic oxide, A synthetic method of acetoxyacetic acid making carbon monoxide, acetic acid, and/or an acetic anhydride react to a compound which generates formaldehyde under formaldehyde and/or a reaction condition into a reaction medium. 2. Synthetic method of acetoxyacetic acid given in the above 1 which is at least one sort chosen from group which sulfuric acid root support

metallic oxide becomes from sulfuric acid root support zirconia, sulfuric acid root support titania, and sulfuric acid root support tin oxide.

3. Synthetic method of acetoxyacetic acid given in the above 1 or 2 which is at least one sort chosen from group which reaction medium becomes from halogenated aliphatic hydrocarbon, halogenated aromatic hydrocarbon, aliphatic hydrocarbon, and aromatic hydrocarbon.

4. Catalyst for composition of acetoxyacetic acid which consists of at least one sort chosen from group which consists of sulfuric acid root support zirconia, sulfuric acid root support titania, and sulfuric acid root support tin oxide.

[0012]

[Embodiment of the Invention]In the synthetic method of acetoxyacetic acid the synthetic method of acetoxyacetic acid concerning this invention, Carbon monoxide, acetic acid, and/or an acetic anhydride are made to react to the compound which generates formaldehyde under formaldehyde and/or a reaction condition under existence of a sulfuric acid root support metallic oxide into a reaction medium.

[0013]The sulfuric acid root support metallic oxide in particular used as a catalyst for composition of acetoxyacetic acid is not restricted, for example, can illustrate sulfuric acid root support zirconia, a sulfuric acid root support titania, sulfuric acid root support tin oxide, etc.

[0014]Although the holding amount in particular of the sulfuric acid root in a sulfuric acid root support metallic oxide is not restricted, it is usually about 1 to 5 % of the weight preferably about 0.5 to 10% of the weight in sulfur conversion to a metallic oxide.

[0015]Although the specific surface area in particular of a sulfuric acid root support metallic oxide is not restricted, it is usually an 80-120-m²/g grade preferably about [50-150 m²/g as measured value by a BET adsorption method.

[0016]What was prepared by the publicly known method may be used for a sulfuric acid root support metallic oxide, and a commercial item may be used for it. A sulfuric acid root support metallic oxide can be prepared using Appl. Catal. A, 146 (1996), the method indicated to 3-32, etc., for example. A starting material can be processed with dilute sulfuric acid, and, specifically, it can prepare by the method of calcinating under oxidizing atmospheres, such as air, etc.

[0017]The starting material of a sulfuric acid root support metallic oxide can be suitably chosen according to a desired sulfuric acid root support metallic oxide. A starting material may be prepared using a publicly known method, and a commercial item may be used for it. For example, when preparing sulfuric acid root support zirconia, zirconium hydroxide etc. can be illustrated as a starting material. Especially zirconium hydroxide can illustrate what it was not restricted, for example, was prepared from zirconium nitrate dihydrate, zirconium oxide chloride 8 hydrate, etc. When preparing a sulfuric acid root support titania, titanium hydroxide etc. can be illustrated as a starting material. Especially titanium hydroxide can illustrate what it was not

restricted, for example, was prepared from titanium tetraisopropoxide etc. When preparing the sulfuric acid root support tin oxide, tin hydroxide can be illustrated as a starting material. Tin hydroxide can illustrate what was prepared, for example from tin tetrachloride 5 hydrate, octylic acid tin, etc.

[0018]Calcination temperature can be suitably chosen according to a desired sulfuric acid root support metallic oxide. Generally the calcination temperature in the case of preparing sulfuric acid root support zirconia is about 500-700 **, and its about 550-650 ** is desirable. Generally the preparation temperature in the case of preparing a sulfuric acid root support titania is about 450-650 **, and is desirable. [of about 500-600 **] The calcination temperature in the case of preparing the sulfuric acid root support tin oxide is about 450-650 **, and its about 500-600 ** is desirable.

[0019]The case where sulfuric acid root support zirconia is prepared from zirconium nitrate dihydrate is mentioned as an example, and a preparing method is explained more concretely. If concentrated ammonia water is added until it becomes pH seven to about eight in zirconium nitrate dihydrate solution, zirconium hydroxide deposits. In the obtained zirconium hydroxide, a washing and ** exception may process desiccation etc. if needed. Under oxidizing atmospheres, such as air, zirconium hydroxide is continuously processed contact, immersion, etc. and calcinated to dilute sulfuric acid at about 500-700 **.

[0020]The synthetic powder used in the synthetic method of this invention will not be limited especially if it is a compound which generates formaldehyde under formaldehyde and/or a reaction condition. As a compound which generates formaldehyde under a reaction condition, a 1,3,5-trioxane, paraformaldehyde, alpha-polyoxymethylene, tetra oxane, etc. can be illustrated, for example. One sort may be independently used for these compounds, and they may use two or more sorts together. Although the quantity in particular of the synthetic powder used for a reaction is not limited, it is usually about 0.5-50 mmol in formaldehyde conversion to 1 g of sulfuric acid root support metal oxide catalysts, and is about 1-5 mmol preferably.

[0021]In the synthetic method of this invention, acetoxycetic acid composition is attained by adding optimum dose of acetic acid and/or acetic anhydrides in a reaction medium. As opposed to the number of mols of the formaldehyde whose addition of acetic acid and/or an acetic anhydride is synthetic powder (the number of mols which was converted at formaldehyde in the case of the compound which generates formaldehyde under a reaction condition), usually, the 100 time mol grade from equimolar -- it is a five to 20 time mol grade preferably.

[0022]Although the reaction medium used by this invention cannot be concerned and can be used for polarity and non-polarity, acetoxycetic acid is obtained with higher yield by using a solvent with fixed polarity. As a reaction medium, aromatic hydrocarbon, such as aliphatic

hydrocarbon, such as halogenated aromatic hydrocarbon, such as halogenated aliphatic hydrocarbon, such as chloroform and dichloromethane, and chlorobenzene, hexane, cyclohexane, and a methylcyclohexane, and benzene, etc. can be illustrated, for example. As a reaction medium, halogenated aliphatic hydrocarbon, such as chloroform and dichloromethane, is preferred in these. One sort may be independently used for a reaction medium, and it may use two or more sorts together.

[0023]Although the reaction pressure in particular in the synthetic method of this invention is not limited, generally it is a 10 - 100 kg/cm² grade as a carbon monoxide partial pressure, and is a 30 - 60 kg/cm² grade preferably.

[0024]Although reaction temperature in particular is not limited, generally it is about 100-170 **, and is about 130-150 ** preferably.

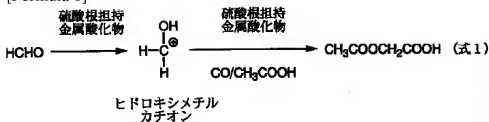
[0025]this invention method can be enforced as follows, for example. After putting formaldehyde, a reaction medium, acetic acid and/or an acetic anhydride, and a sulfuric acid root support metallic oxide into autoclave and purging with carbon monoxide if needed, the carbon monoxide of a predetermined pressure is introduced. What was diluted with inactive gas, such as rare gas and nitrogen, may be used for the carbon monoxide to introduce. Stirring, temperature up is carried out and it is made to react preferably fixed time to a predetermined temperature for about 1 to 4 hours. The mixed liquor of acetoxycetic acid and a solvent is obtained after ending reaction by a ** exception carrying out the sulfuric acid root support oxide which is a catalyst from a reaction mixture. although the total pressure in particular of a reaction is not restricted -- usually -- 10 kg/cm² - a 150 kg/cm² grade -- they are 30 kg/cm² - a 70 kg/cm² grade preferably.

[0026]Separation of the output from mixed liquor can be performed using publicly known methods, such as extraction and recrystallization. Specifically, the following procedures can be illustrated. If decompression runoff of the reaction medium is carried out from the obtained filtrate after removing a sulfuric acid root support metallic oxide by filtering a reaction mixture, the oil containing an object will be obtained. An object is separable by presenting methods, such as preparative gas chromatography, preparative isolation high performance chromatography, and distillation under reduced pressure, with the obtained oil.

[0027]It is thought with the synthetic method of this invention that acetoxycetic acid generates as follows. According to a sulfuric acid root support metal oxide catalyst, formaldehyde is changed into a hydroxymethyl cation, and when acetic acid or the acetic anhydride which exists in carbon monoxide and the system of reaction continuously reacts, it gives acetoxycetic acid of output. The reaction formula in the case of reacting the bottom of existence of a sulfuric acid root support metal oxide catalyst to the formula 1, making carbon monoxide and acetic acid react to formaldehyde, and compounding acetoxycetic acid is shown.

[0028]

[Formula 1]



[0029]

[Effect of the Invention] According to this invention, acetoxyacetic acid can be selectively obtained with high yield under milder temperature and pressure conditions.

[0030] According to this invention, acetoxyacetic acid can be obtained to ** high yield, without using strong acid and the expensive solid acid of a fluid by using a sulfuric acid root support metallic oxide composition being easy and comparatively cheap as a catalyst.

[0031] Since the catalyst of this invention is solid super-strong acid, separation of the catalyst from output is easy for it. Therefore, the synthetic method of more economical acetoxyacetic acid can be provided.

[0032]

[Example] Hereafter, an example explains this invention in detail.

[0033] The aqueous ammonia solution was added 25% until it dissolved 200 g of example 1 zirconium-nitrate dihydrate in the water of 5L and was set to pH 8. After the water (50-60 ** warm water) of 3L washed the depositing solid, 115 g of zirconium hydroxide was obtained by a ** exception's carrying out a solid and drying it at 100 ** for 24 hours. It was air-dry overnight, after contacting 30 ml of 1N sulfuric acid to 2 g of zirconium hydroxide on a filter paper. After putting this into the glass sample pipe and calcinating at 600 ** for 3 hours, sulfuric acid root support zirconia was obtained by carrying out the sealed tube at the time of heat.

[0034] After putting the sulfuric acid root support zirconia prepared from 2 g of zirconium hydroxide, 1,3,5-trioxane 5mmol, 50 ml of dichloromethane, and acetic acid 50mmol into autoclave and purging with carbon monoxide, the carbon monoxide of 50 kg/cm² was introduced. The glass tube which carried out the sealed tube of the sulfuric acid root support zirconia exploded by this pressure. Stirring, temperature up was carried out and it was made to react to 150 ** for 3 hours.

[0035] The ** exception carried out the reaction mixture and the catalyst after ending reaction. Distillation under reduced pressure of the filtrate was carried out, and it was condensed. What diluted a part of this concentrate with the solvent was used for the following analysis. Gas chromatography (GC), gas chromatography mass (GC-MS) analysis, and NMR measurement were performed. As a result, the main output was identified acetoxyacetic acid. GC analysis which used n-heptadecane for the internal standard substance performed a fixed

quantity of acetoxyacetic acid, and it checked that the yield was 60%.
 [0036]As example 2 catalyst, the sulfuric acid root support zirconia prepared like Example 1 was used. After putting the sulfuric acid root support zirconia prepared from 2g of zirconium hydroxide, 1,3,5-trioxane 5mmol, 50 ml of dichloromethane, and acetic acid 50mmol into autoclave and purging with carbon monoxide, the carbon monoxide of 50 kg/cm² was introduced. Stirring, temperature up was carried out and it was made to react to 110 °C for 3 hours.

[0037]The exception carried out the reaction mixture and the catalyst after ending reaction. As a result of conducting the same analysis as Example 1, it checked that the yield of acetoxyacetic acid which is the main output was 13%.

[0038]As example 3 catalyst, the sulfuric acid root support zirconia prepared like Example 1 was used. After putting the sulfuric acid root support zirconia prepared from 2g of zirconium hydroxide, 1,3,5-trioxane 1.7mmol, 50 ml of cyclohexane, and acetic acid 50mmol into autoclave and purging with carbon monoxide, the carbon monoxide of 50kg/cm² was introduced. Stirring, temperature up was carried out and it was made to react to 150 °C for 3 hours.

[0039]The exception carried out the reaction mixture and the catalyst after ending reaction. As a result of conducting the same analysis as Example 1, it checked that the yield of acetoxyacetic acid which is the main output was 3.5%.

[0040]As example 4 catalyst, the sulfuric acid root support zirconia prepared like Example 1 was used. After putting the sulfuric acid root support zirconia prepared from 2g of zirconium hydroxide, 1,3,5-trioxane 1.7mmol, 50 ml of benzene, and acetic acid 50mmol into autoclave and purging with carbon monoxide, the carbon monoxide of 50 kg/cm² was introduced. Stirring, temperature up was carried out and it was made to react to 150 °C for 3 hours.

[0041]The exception carried out the reaction mixture and the catalyst after ending reaction. As a result of conducting the same analysis as Example 1, it checked that the yield of acetoxyacetic acid which is the main output was 3.0%.

[0042]As example 5 catalyst, the sulfuric acid root support zirconia prepared like Example 1 was used. After putting the sulfuric acid root support zirconia prepared from 2g of zirconium hydroxide, 1,3,5-trioxane 1.7mmol, 50 ml of chlorobenzene, and acetic acid 50mmol into autoclave and purging with carbon monoxide, the carbon monoxide of 50 kg/cm² was introduced. Stirring, temperature up was carried out and it was made to react to 150 °C for 3 hours.

[0043]The exception carried out the reaction mixture and the catalyst after ending reaction. As a result of conducting the same analysis as Example 1, it checked that the yield of acetoxyacetic acid which is the main output was 13%.

[0044]As example 6 catalyst, the sulfuric acid root support zirconia prepared like Example 1 was used. After putting the sulfuric acid root support zirconia prepared from 2g of zirconium hydroxide, 1,3,5-

trioxane 5mmol, 50 ml of dichloromethane, and acetic anhydride 5mmol into autoclave and purging with carbon monoxide, the carbon monoxide of 50 kg/cm² was introduced. Stirring, temperature up was carried out and it was made to react to 150 °C for 3 hours.

[0045]The ** exception carried out the reaction mixture and the catalyst after ending reaction. As a result of conducting the same analysis as Example 1, it checked that the yield of acetoxyacetic acid which is the main output was 33%.

[0046]As [example 7](#) catalyst, the sulfuric acid root support zirconia prepared like Example 1 was used. The sulfuric acid root support zirconia prepared from 2g of zirconium hydroxide to autoclave, After putting in 5mmol, 50 ml of dichloromethane, and acetic acid 50mmol by formaldehyde conversion and purging paraformaldehyde with carbon monoxide, the carbon monoxide of 50kg/[cm]² was introduced. Stirring, temperature up was carried out and it was made to react to 150 °C for 3 hours.

[0047]The ** exception carried out the reaction mixture and the catalyst after ending reaction. As a result of conducting the same analysis as Example 1, it checked that the yield of acetoxyacetic acid which is the main output was 32%.

[0048]Composition of acetoxyacetic acid was tried without using [comparative example 1](#) reaction medium. As a catalyst, the sulfuric acid root support zirconia prepared like Example 1 was used. After putting into autoclave sulfuric acid root support zirconia and 1,3,5-trioxane 5mmol and acetic acid 50mmol which were prepared from 2g of zirconium hydroxide and purging with carbon monoxide, the carbon monoxide of 50 kg/cm² was introduced. Stirring, temperature up was carried out and it was made to react to 150 °C for 3 hours.

[0049]The ** exception carried out the reaction mixture and the catalyst after ending reaction. As a result of conducting the same analysis as Example 1, it checked that acetoxyacetic acid was not generating at all.

[0050]145 ml of [example 8](#) titanium tetraisopropoxide was put into the water of 2L, and 125 ml of nitric acid was added 60% continuously. In addition, the water of 5L washed the depositing solid until the aqueous ammonia solution was set to pH 8 25%. 43 g of titanium hydroxide was obtained by drying the obtained solid at 100 °C for 24 hours. It was air-dry overnight, after contacting 30 ml of 1N sulfuric acid on a filter paper to the titanium hydroxide 2g. After putting this into the glass tube and calcinating at 550 °C for 3 hours, the sulfuric acid root support titania was obtained by carrying out the sealed tube.

[0051]After putting the sulfuric acid root support titania prepared from the titanium hydroxide 2g, 1,3,5-trioxane 1.7mmol, 50 ml of dichloromethane, and acetic acid 50mmol into autoclave and purging with carbon monoxide, the carbon monoxide of 50 kg/cm² was introduced. The glass sample pipe which carried out the sealed tube of the sulfuric acid root support titania exploded with this pressure. Stirring, temperature up was carried out and it was made to react to 150

** for 3 hours.

[0052]The ** exception carried out the reaction mixture and the catalyst after ending reaction. As a result of conducting the same analysis as Example 1, it checked that the yield of acetoxycetic acid which is the main output was 31%.

[0053]The example 9 tin-tetrachloride 5 hydrate 50g was dissolved in the water of 1L, and the aqueous ammonia solution was added 25% until it was set to pH 9.5-10. After the water of 5L washed the depositing solid, 13 g of tin hydroxide was obtained by a ** exception's carrying out a solid and drying it at 100 ** for 24 hours. The dipping of the tin hydroxide 2g and 30 ml of the 6N sulfuric acid was stirred and carried out for 30 minutes in the beaker. After the ** exception's having carried out the solid, putting into the glass tube what was air-dried overnight and calcinating at 550 ** for 3 hours, the sulfuric acid root support tin oxide was obtained by carrying out the sealed tube.

[0054]After putting the sulfuric acid root support tin oxide prepared from the tin hydroxide 2g, 1,3,5-trioxane 1.7mmol, 50 ml of dichloromethane, and acetic acid 50mmol into autoclave and purging with carbon monoxide, the carbon monoxide of 50 kg/cm² was introduced. Stirring, temperature up was carried out and it was made to react to 150 ** for 3 hours.

[0055]The ** exception carried out the reaction mixture and the catalyst after ending reaction. As a result of conducting the same analysis as Example 1, the yield of acetoxycetic acid which is the main output checked that it was 48%.

[Translation done.]

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最終頁に続く

(54) 【発明の名称】 羧酸根相持金属酸化物を触媒とするアセトキシ酢酸の合成法

(57) 【要約】

【課題】 より簡易に、より穏和な条件下において、経済的にアセトキシ酢酸を合成する方法を提供する。

【解決手段】 アセトキシ酢酸の合成法において、羧酸根相持金属酸化物の存在下、ホルムアルデヒドおよび/または反応条件下においてホルムアルデヒドを生成する化合物に、一酸化炭素と酢酸および/または無水酢酸とを反応媒体中において反応させることを特徴とするアセトキシ酢酸の合成法。

中で反応させヒドロキシカルボン酸誘導体を得ることを特徴とするヒドロキシカルボン酸誘導体の製造方法」が開示されている。上記公報には、ヒドロキシカルボン酸としてアセトキシ酢酸が合成できることが開示されてい

成法は、アセトキシ酢酸の合成法において、硫酸根担持金属酢酸化物の存在下、ホルムアルデヒドおよび/または反応条件下においてホルムアルデヒドを生成する化合物に、一酸化炭素と酢酸および/または無水酢酸とを反応

50

媒体中において反応させることを特徴とする。

【0013】アセトキシ酢酸の合成用触媒として用いる硫酸根担持全金属化合物は、特に制限されず、例えば、硫酸根担持シリコニア、硫酸根担持チタニア、硫酸根担持酸化スズなどを例示することができる。

【0014】硫酸根担持金属酸化物における硫酸根の担持量は、特に制限されないが、金属酸化物に対して、硫酸換算で通常0.5~10重量%程度、好ましくは1~5重量%程度である。

【0015】硫酸根担持金属酸化物の比表面積は、特に制限されないが、BET法による測定値として、通常90~150m²/g程度、好ましくは80~120m²/g程度である。

【0016】 碱酸根担持金属酸化物は、公知の方法によって調製したものを用いてもよく、市販品を用いてもよい。碱酸根担持金属酸化物は、例えば、Appl. Catal. A, 146(1996)、3-32に記載されている方法などを用いて調製することができる。具体的には、出発物質を希硫酸で処理し、空気などの酸化雰囲気下において焼成する方法などによって調製することができる。

【0017】硫酸根担持金属酸化物の発出物質は、希望の硫酸根担持金属酸化物に依って適宜選択することができる。発出物質は、公知の方法を用いて調製してもよく、市販品を用いてもよい。例えば、硫酸根担持シリコンを調製する場合は、発出物質として、水酸化シリコンウムなどを示すことができる。水酸化シリコンウムは、特に制限されず、例えばは硫酸シリコンウム二水和物、塩化酸シリコンウム八水和物などから調製したものなどを示すことができる。硫酸根担持チタンを調製する場合は、発出物質として、水酸化チタンなどを示すことができる。水酸化チタンは、特に制限されず、例えばはチタートライソプロポキシドなどから調製したものなどを示すことができる。硫酸根担持酸化スズを調製する場合は、発出物質として、水酸化スズを示すことができる。水酸化スズは、例えばは四酸化スズ五水和物、オクチル酸スズなどから調製したものなどを示すことができる。

【0018】焼成温度は、所望の炭酸根担持金属酸化物に応じて適宜選択することができる。炭酸根担持シリコニアを調製する場合の焼成温度は、一般に500～700℃程度であり、550～650℃程度が望ましい。炭酸根担持チタニアを調製する場合の調製温度は、一般に450～650℃程度であり、500～600℃程度が望ましい。炭酸根担持酸化スズを調製する場合の焼成温度は、450～650℃程度であり、500～600℃程度が望ましい。

【0019】硝酸ジルコニウム二水和物から硫酸根担持ジルコニアを調製する場合を例に挙げて、調製方法をより具体的に説明する。硝酸ジルコニウム二水和物水溶液にpH7~8程度になるまで濃アンモニア水を加えると、水酸化ジルコニウムが析出する。得られた水酸化ジルコニ

漬などの処理を施し、続いて空気などの酸化雰囲気下において500～700℃程度で焼成する。

【0120】本発明の合成法において用いる合成原料は、ホルムアルデヒドおよび/または反応条件下においてホルムアルデヒドを生成する化合物であれば特に限定されない。反応条件下においてホルムアルデヒドを生成する化合物としては、例えば、1,3,5-トリオキサン、パラホルムアルデヒド、 α -ポリオキシメチレン、テトラオキサンなどを例示できる。これらの化合物は、1価を単独で用いても良く、2価以上を併用しても良い。反応に使用する合成原料の量は、特に限定されないが、流酸相持増全原酸化物触媒1gに対して、ホルムアルデヒド換算で通常0.5~9mmol程度であり、好ましくは1~5mmol程度である。

【0121】本発明の合成法においては、反応媒体中に適量の酢酸および/または無水酢酸を添加することによってアセトキシ生成反応が可能となる。酢酸および/または無水酢酸の添加量は、合成原料であるホルムアルデヒドのモル数(反応条件下においてホルムアルデヒドを生成する化合物の場合にはホルムアルデヒドに換算したモル数)に対して、通常等モルから100倍モル程度、好ましくは5〜200倍モル程度である。

【0122】本発明で使用される反応媒体は、極性、非極性に問わず使用できるが、一定の極性を持つ溶媒を使用することによって、より高い収率でアセトキシ酢酸が得られる。反応媒体として、例えば、クロロホルム、ジクロロメタンなどのハロゲン化脂肪族炭化水素、クロロベンゼン等のハロゲン化芳香族炭化水素、ヘキサン、シクロヘキサン、メチルシクロヘキサン等の脂肪族炭化水素、ベンゼン等の芳香族炭化水素などを示すことができる。反応媒体としては、これらの中では、クロロホルム、ジクロロメタンなどのハロゲン化脂肪族炭化水素が好ましい。反応媒体は、1種を単独で用いても良く、2種以上を併用しても良い。

【0023】本発明の合成法における反応圧力は、特に限定されるものではないが、一般に一酸化炭素分圧として10~100kg/cm²程度であり、好ましくは30~60kg/cm²程度である。

【0024】反応温度は特に限定されるものではないが、一般に160~170℃程度であり、好ましくは130~150℃程度である。

【0125】本発明方法は、例えば以下のようにして実施することができる。オートクレーブにホルムアルデヒド、反応媒体、酢酸および/または無水酢酸並びに硫酸根持全金属酸化物を入れ、必要に応じて一酸化炭素をパージした後、所定の圧力の一酸化炭素を導入する。導入した一酸化炭素は、希ガス、窒素などの不活性ガスで希釈したものを用いてもよい。密封しながら所定の温度で希

にpH7～8程度になるまで濃アンモニア水を加えると、水酸化ジルコニウムが析出する。得られた水酸化ジルコニウムには、必要に応じて、洗浄、濾別、乾燥などの処理をしてもよい。水酸化ジルコニウムを希硫酸に接触、浸

する一酸化炭素は、希ガス、窒素などの不活性ガスで希釈したものを用いてもよい。維持しながら所定の温度まで昇温し、一定の時間、好ましくは1～4時間連続反応させる。反応終了後、反応混合物から触媒である硫酸根

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は、この圧力で破裂した。攪拌しながら、156℃まで昇
温し、3時間反応させた。

【0035】反応終了後、反応混合物と触媒とをろ別し
た。ろ液を減圧蒸留し濃縮した。この濃縮液の一部を溶

た。

【0040】実施例4

触媒として、実施例1と同様に調製した硫酸根担持シル
コニアを用いた。オートクレーブに水酸化ジルコニウム

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特開 2 0 0 1 - 3 3 5 5 3 8

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